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# Gold nanoparticle ensembles as heaters and actuators: melting and collective plasmon resonances

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**Abstract** We describe the peculiar conditions under which optically driven gold nanoparticles (NPs) can significantly increase temperature or even melt a surrounding matrix. The heating and melting processes occur under light illumination and involve the plasmon resonance. For the matrix, we consider water, ice, and polymer. Melting and heating the matrix becomes possible if a nanoparticle size is large enough. Significant enhancement of the heating effect can appear in ensembles of NPs due to an increase of a volume of metal and electric-field amplification.

**Keywords** Metal nanoparticles · Heat generation · Plasmons

There has been a great deal of interest in recent years in the development of biosensors and actuators based on metal and semiconductor nanoparticles (NPs). Metal NPs can efficiently quench [1] or enhance [2] photoluminescence from attached quantum emitters. The latter has been demonstrated for bio-conjugates composed of Au NPs, linker molecules, and semiconductor nanocrystals. Metal (gold) NPs have useful thermal properties. Under optical illumination, Au NPs efficiently create heat [3–8]. The heating

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effect becomes especially strong under the plasmon resonance conditions when the energy of incident photons is close to the plasmon frequency of an Au NP. In recent papers, the heating effect in Au NPs was used for several purposes. The paper [3] reports imaging of proteins labeled with Au NPs in cells, using an all-optical method based on photo-thermal interference contrast. In the paper [4] the heating effect from gold NPs is used for biomedical applications. Another publication [5] described remote release of materials (drugs) from a capsule containing Au NPs excited with intense light. In the paper [7], the authors assembled a superstructure Au-NP-polymer-CdTe-NP with interesting thermal properties. Due to the exciton-plasmon interaction, the optical emission of such a superstructure is strongly temperature-dependent [7]. The study [8] characterized heat generation due to gold NPs at the nanoscale level through the observation of the melting process in the ice matrix. In particular, it was found in Ref. [8] that the heating process has a mesoscopic character and strongly depends on the geometry of a NP ensemble.

Here we study theoretically the processes of heating and melting due to single Au NPs and NP complexes. We find the conditions and estimate the typical times to significantly increase the temperature of the surrounding material. Our estimations show that using accessible light intensities one can melt ice or polymer matrixes around a single Au NP. The polymer is very common in modern nanotechnology and has properties analogous to the biological matter. Therefore, our results can be useful to understand and design heating effects of Au NPs embedded into biological and living systems. The ice is a very convenient model system which can be easily prepared and controlled. This system can be used

to study experimentally mechanisms of heat generation and transfer on nanoscale [8]. Here, we also describe how to enhance the heating effects. For this, one can use a collection of Au NPs where the heating enhancement can come from the following factors: (1) heat fluxes from different NPs can be added and (2) the light-induced electric field inside a superstructure under certain conditions can be strongly enhanced due to collective plasmon resonances.

#### **General equations**

In the absence of phase transformations, heat transfer in a system with NPs is described by the usual heat transfer equation:

$$\rho(\mathbf{r})c(\mathbf{r})\frac{\partial T(\mathbf{r},t)}{\partial t} = \nabla k(\mathbf{r})\nabla T(\mathbf{r},t) + Q(\mathbf{r},t), \tag{1}$$

where  $T(\mathbf{r},t)$  is temperature as a function of coordinate  $\mathbf{r}$  and time t,  $\rho(\mathbf{r})$ ,  $c(\mathbf{r})$  and  $k(\mathbf{r})$  are the mass density, specific heat, and thermal conductivity, respectively. The local heat intensity  $Q(\mathbf{r},t)$  comes from light dissipation in Au NPs:

$$Q(\mathbf{r},t) = \langle \mathbf{j}(\mathbf{r},t) \cdot \mathbf{E}(\mathbf{r},t) \rangle_{t} = -\frac{1}{2} \operatorname{Re} \left[ i\omega \frac{\varepsilon(\mathbf{r}) - 1}{4\pi} \tilde{\mathbf{E}}(\mathbf{r}) \tilde{\mathbf{E}}^{*}(\mathbf{r}) \right],$$
(2)

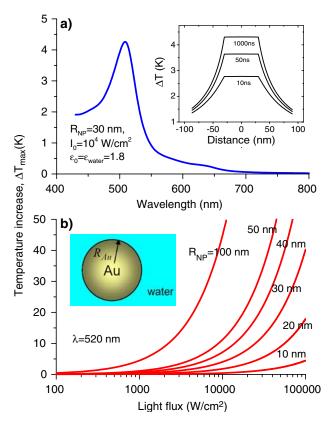
where  $\mathbf{j}(\mathbf{r},t)$  is the current density,  $\mathbf{E}(\mathbf{r},t) = \mathrm{Re}\left[\tilde{\mathbf{E}}(\mathbf{r}) \cdot e^{-i\omega t}\right]$  is the resulting electric field in the system, and  $\varepsilon(\mathbf{r})$  is the dielectric constant. Here we assume that the system is excited with the external laser field  $\mathbf{E}_0(t) = \mathrm{Re}\left[\tilde{\mathbf{E}}_0(t) \cdot e^{-i\omega t}\right]$ . If light is turned on at t=0, the light intensity is given by  $I(t) = I_0 = c\mathbf{E}_0^2 \sqrt{\varepsilon_0}/8\pi$  for t>0 and 0 at t<0. Here  $\varepsilon_0$  is the dielectric constant of matrix.

## Heating of water due to a single NP

We first consider a single spherical NP of radius  $R_{\rm NP}$  and dielectric constant  $\varepsilon_m(\omega)$  (see inset in Fig. 1b). For this case, the time-dependent solution of Eq. 1 is known [6, 9]. In the limit  $t \to \infty$ , the temperature distribution outside the NP is given by a simple equation:

$$\Delta T(\mathbf{r}) = \frac{V_{\rm NP}Q}{4\pi k_0} \frac{1}{r} (r > R_{\rm NP}), \tag{3}$$

where  $k_0$  is the thermal conductivity of water. The rate of heat dissipation Q depends on the induced electric field inside Au NP and is given by the equation



**Fig. 1** Calculated temperature increase at the surface of Au NP in the water as a function of wavelength (a) and illumination power (b). The graph (b) is given at the plasmon peak wavelength. A matrix is the water with  $\varepsilon_0 = 1.8$ . Inset: spatial distribution of temperature at different times

$$Q = -\text{Re}\left[i\omega\frac{\varepsilon(\mathbf{r}) - 1}{8\pi}\mathbf{E}_0^2 \left| \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_m} \right|^2\right].$$

To calculate the local heat Q, we used the equation  $\tilde{\mathbf{E}}(\mathbf{r}) = [3\varepsilon_0/(2\varepsilon_0 + \varepsilon_m)]\mathbf{E}_0$  for  $r < R_{\rm NP}$  [10]. The maximum temperature increase occurs at  $r = R_{\rm NP}$ :

$$\Delta T_{\text{max}}(I_0) = \frac{R_{\text{NP}}^2}{3k_0} \text{Re} \left[ i\omega \frac{1 - \varepsilon(\mathbf{r})}{8\pi} \left| \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_m} \right|^2 \right] \frac{8\pi \cdot I_0}{c\sqrt{\varepsilon_0}},$$
(4)

where  $I_0$  is the light intensity inside the matrix. Figure 1 shows calculated  $\Delta T_{\rm max}(I_0,R_{\rm NP})$  using the dielectric constant of bulk Au [11]. We see from Eq. 4 that in order to achieve a visible heating effect of a few K for typical light fluxes  $10^3-10^6$  W/cm², one should use NPs of relatively large radius ( $\geq 10$  nm). The flux  $2 \cdot 10^5$  W/cm² corresponds to the laser power of 25 mW and the laser spot diameter of 4  $\mu$ m. The time dynamic of heating for the case of water and Au NP is relatively fast. At time  $t \approx 10$  ns the temperature  $\Delta T(r = 0)$  rises to  $\Delta T_{\rm max}/2$  (see inset of Fig. 1a). This characteristic



time can be estimated as  $t = \tau_0 = R_{\rm NP}^2(c_0\rho_0/k_{t0}) \approx 6$  ns for  $R_{\rm NP}$ =30 nm. For  $t\gg\Delta t_{\rm Au}$ , we can obtain an useful asymptotic formula:

$$\Delta T_{\max}(t, I_0) = \Delta T_{\max}(I_0) \left[ 1 - \frac{1}{\sqrt{\pi t/\tau_0}} \right].$$

We note that the thermal diffusion time in the gold NP,  $\Delta t_{\rm Au} = R_{\rm NP}^2/K_{\rm Au}$ , is much shorter than that in the water. Here  $K_{\rm Au} = k_{t~\rm Au}/c_{\rm Au}\rho_{\rm Au}$  is the thermal diffusivity of gold.

## Melting of ice matrix due to a single NP

Heat flowing from an optically driven Au NP can melt the matrix. In this case, the matrix around the NP becomes inhomogeneous in space and is described by the dielectric constant  $\varepsilon_0(\mathbf{r})$  and thermal conductivity  $k_0(\mathbf{r})$ . In the case of infinite matrix, our model should now include a spherical shell of liquid around the NP (Fig. 2a). For the three regions (Au, liquid, and solid), we obtain the following stationary solutions  $(t \to \infty)$ :

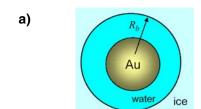
$$\Delta T_{\rm Au}(r) = A - \frac{Q \cdot r^2}{6k_{\rm Au}}, \quad \Delta T_{\rm liquid}(r) = B + \frac{C}{r},$$

$$\Delta T_{\rm solid}(r) = \frac{D}{r},$$
(5)

where A,B,C, and D are unknown coefficients. Temperature and energy flux,  $k_t(r)\cdot dT(r)/dr$ , at the interfaces should be continuous. From these boundary conditions we obtain expressions for the coefficients in Eq. 5. For example,  $D = \frac{QR_{\text{Aul}}^3}{3k_{\text{solid}}}$ . To find the position of the solid–liquid boundary  $(R_{\text{b}})$ , we have to solve the equation:  $\Delta T(r) + T_0 = T_{\text{trans}}$ , where  $T_0 = T(r \to \infty)$  is the equilibrium temperature of matrix and  $T_{\text{trans}}$  is the phase transition temperature. Then, we obtain:

$$R_{\rm b} = \frac{D}{T_{\rm trans} - T_0} = \frac{QR_{\rm Au}^3}{3k_{\rm solid}(T_{\rm trans} - T_0)}.$$

Figure 2b shows calculated spatial distribution of temperature for the case of ice matrix at  $T_0$ =  $-2^{\circ}$ C. The inset of Fig. 2b includes the data for the water–ice boundary ( $R_b > 30$  nm). Melting occurs for  $Q > Q_{\rm melting}$ ; this condition can also be written as  $R_b > R_{\rm Au}$  or  $\frac{QR_{\rm Au}^2}{3(T_{\rm trans}-T_0)} > k_{\rm solid}$ . In other words, heat generated by the NP should exceed heat diffusion in the ice. For the given parameters, melting occurs at light fluxes  $I_0 > 1.3 \cdot 10^4$  W/cm². The parameters of the ice—water matrix are the following:  $T_{\rm trans} = 0^{\circ}$ C,  $k_{t,\rm water} = 0.6$  W/mK, and  $k_{t,\rm ice} = 1.6$  W/mK.



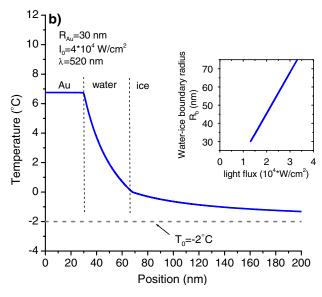


Fig. 2 (a) Model of Au NP and melted ice matrix. (b) Calculated temperature as a function of coordinate. Inset: the radius of water–ice interface as a function of the light flux. A matrix is described with  $\epsilon_{water}{\approx}\epsilon_{ice}=\epsilon_0=1.8$ .

In the next step we are going to estimate the time to melt ice around a NP. For this, we calculate the amount of heat needed to melt ice and increase its temperature. The time to establish steady state within the volume  $0 < r < R_{\rm max}$ can be estimated as

$$\begin{split} \Delta t_{\text{melting}} &= \frac{1}{V_{\text{NP}}Q} \bigg\{ c_{\text{Au}} \rho_{\text{Au}} \int_{\text{Au}} \Delta T_{\text{Au}}(r) \text{d}V \\ &+ L_{\text{ice}} \rho_{\text{ice}} V_{\text{ice}} + c_{\text{ice}} \rho_{\text{ice}} (T_{\text{trans}} - T_0) V_{\text{ice}}. \\ &+ c_{\text{w}} \rho_{\text{w}} \int_{\text{water}} \Delta T_{\text{w}}(r) \text{d}V + c_{\text{ice}} \rho_{\text{ice}} \int_{\text{ice}, R_{\text{b}} < r < R_{\text{max}}} \Delta T_{\text{ice}}(r) \text{d}V \bigg\}, \end{split}$$

$$\tag{6}$$

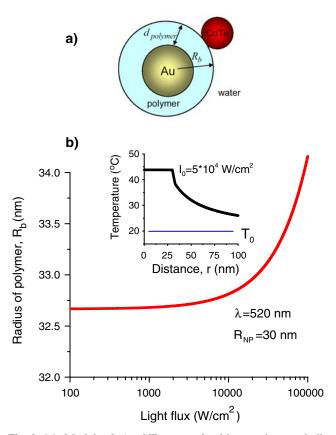
where  $V_{\rm ice}$  is the volume of melted ice. Note that the upper limit  $r = R_{\rm max}$  should be kept finite since the integral is not converging. We will choose  $R_{\rm max}$  large enough so that  $R_{\rm max} > R_{\rm b}$ . This insures us that the melting process is accomplished at  $t < \Delta t_{\rm melting}$  and simultaneously the steady state is established in the spatial region  $r < R_{\rm max}$ . The time  $\Delta t_{\rm melting}$  is relatively long because of a large latent heat needed to melt ice.



This time  $\Delta t_{\rm melting}$  is much longer than the characteristic heat-diffusion times,  $R_i^2/K_i = R_i^2 \cdot (\rho_i c_i/k_i)$ , in metal, ice, and water:  $\Delta t_{\rm metal} = (30 \text{ nm})^2/K_{\rm Au} \approx 7 \text{ ps}$ ,  $\Delta t_{\rm ice} \approx (40 \text{ nm})^2/K_{\rm ice} \approx 2 \text{ ns}$ ,  $\Delta t_{\rm water} \approx (40 \text{ nm})^2/K_{\rm water} \approx 10 \text{ ns}$ . For  $R_{\rm max} = 100 \text{ nm}$ , the times  $\Delta t_{\rm melting}$  estimated from Eq. 6 are in the sub-ms-range in the regime of plasmon resonance ( $\lambda \approx 500 \text{ nm}$ ).

## Melting of a polymer shell due to a single Au NP

We now consider an Au NP covered with polymer (Fig. 3a). In this system, heat released from the Au NP can melt the polymer coating. First we are going to consider a model of thin polymer shell including one monolayer of molecules. As an example we describe melting of one monolayer of the PEG polymer; this polymer was used to assemble Au-NP complexes in Ref. [7]. The linear size of such polymer changes



**Fig. 3** (a) Model of Au NP covered with a polymer shell. Emission of an attached semiconductor (CdTe) NP can change as the polymer size melts. This is an example of an actuator. (b) Calculated radius of polymer shell as a function of light intensity;  $T_0 = 20$ °C,  $k_{\rm Au} = 318$  W/mK,  $k_{\rm water} = 0.6$  W/mK, and  $k_{\rm polymer} = 0.2$  W/mK. Inset: Temperature as a function of coordinate for a given light intensity

rapidly in the temperature region  $20\text{--}60^{\circ}\text{C}$  [12] due to the conformation transition and we will approximate its linear size as  $d_{\text{polymer}} = 3 \text{ nm} + (T - 30^{\circ})/30^{\circ}$ . This formula gives 1.3 nm change of polymer length as temperature increases from  $20^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ . For this problem, we can apply the formulas (5) and find the position of the polymer–water interface as a function of light flux:

$$R_{\rm b} = R_{\rm Au} + d_{\rm polymer}[T(R_m)], \tag{7}$$

where  $R_m = R_{\rm Au} + d_{\rm polymer}/2$ . To write the above equation we assumed that the polymer "feels" an averaged temperature equal to the temperature in the middle of the polymer shell at the position  $r = R_m = R_{\rm Au} + d_{\rm polymer}/2$ . The closed equation for  $R_{\rm b}$  becomes

$$R_{\rm b} = R_{\rm Au} + d_{\rm polymer}[T_0 + B(R_{\rm b}) + \frac{C(R_{\rm b})}{R_{\rm Au} + \frac{R_{\rm b} - R_{\rm Au}}{2}}].$$
 (8)

In Fig. 3 we show a calculated radius of polymer shell  $R_b$  as a function of light intensity. These data demonstrate that the Au-NP with a polymer shell can be used as an actuator. Assume now that a CdTe NP is attached to the polymer shell, as it was realized experimentally in recent paper [7]. The intensity of photoluminescence (PL) and energy-dissipation rate of CdTe NP strongly depend on the distance between the CdTe NP and the Au surface. In Ref. [7], it was found that the intensity of PL decreases with the distance  $R_{\rm b}$ and can be approximated by a simple formula  $A + B/R_{\text{CdTeNP}}^{6}$ , where the position of the CdTe NP with respect to the center of Au NP. Regarding nonradiative energy losses of exciton in a CdTe NP, it is known that, for the dipole-surface interaction, the energy-dissipation rate decreases as  $1/d_{polymer}^4$  [13]. Since the polymer size increases with the light intensity via the heating mechanism, PL spectra of the CdTepolymer-Au complex can strongly change with intensity of light. A similar mechanism was recently involved to explain the data of Ref. [7]. In particular, the authors of Ref. [7] varied periodically temperature and observed a periodic variation of PL emission from the CdTe-polymer-Au complex. If the heating effect is induced by light pulses, the size of polymer and the emission of CdTe NP can be changed in time. For the thermal diffusion time in such a complex, we obtain  $R_{
m Au}^2(
ho_{
m polymer}c_{
m polymer}/k_{
m polymer}) pprox 5~{
m ns.}$  To make the above estimate, we used the typical parameters of polymers from Refs. [14] and [15]:  $L_{\text{polymer}} = 200 \text{ KJ/}$ kg,  $\rho_{\text{polymer}} = 1000 \text{ kg/m}^3$ ,  $c_{\text{polymer}} = 1000 \text{ kJ/kg K}$ , and  $k_{\text{polymer}} = 0.2 \text{ W/mK}.$ 

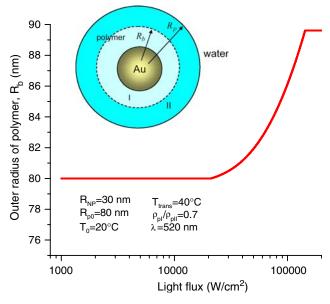


In the next step, we consider an Au NP with a thicker polymer shell. In this case, we can introduce two phases in the polymer shell, melted and non-melted. These phases are shown in inset of Fig. 4 as phases I and II. Again we write equations for  $\Delta T_i(r)$  for each spherical shell and apply the boundary conditions at each interface. The radii of the interfaces ( $R_b$  and  $R_p$ ) should be found from the equations:

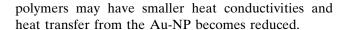
$$\begin{split} & \Delta T(R_{\rm b}) + T_0 = T_{\rm trans}, \\ & \left(R_{\rm p0}^3 - R_{\rm Au}^3\right) \rho_{\rm pII} = \left(R_{\rm b}^3 - R_{\rm Au}^3\right) \rho_{\rm pI} + \left(R_{\rm p}^3 - R_{\rm b}^3\right) \rho_{\rm pII}, \end{split} \tag{9}$$

where  $R_{\rm p0}$  is the polymer outer radius for the non-melted phase and  $\rho_{\rm pI(II)}$  are the polymer densities. The first equation describes the boundary between phases I and II. The second comes from conservation of total number of molecules in the polymer shell and includes the polymer densities,  $\rho_{\rm pI}$  and  $\rho_{\rm pII}$ . The melted polymer has typically a smaller density and therefore the size of the polymer shell increases as polymer melts. The size of polymer as a function of light intensity is show in Fig. 4. Again we observe that the polymer size increases with increasing light intensity. The times to melt the polymer lie in the ms-regime.

In the end of this section, we should also note that the heating effect from the Au NP coated with a polymer can be stronger than that in water because



**Fig. 4** Calculated outer radius of polymer shell as a function of light intensity;  $k_{\rm Au} = 318 \text{ W/mK}$ ,  $k_{\rm water} = 0.6 \text{ W/mK}$ , and  $k_{\rm polymerI} = k_{\rm polymerII} = 0.2 \text{ W/mK}$ . Inset: Model of Au NP with a partially melted polymer shell



#### Heating in an ensemble of NPs

Au NPs can be assembled. For example, the paper [2] reports assembly of Au NPs and CdTe nanowires in cylindrical complexes where Au NPs play a role of photonic amplifier. Putting several Au NPs together can result in stronger enhancement of thermal effects since heat fluxes from individual NPs can be added. If the distance between NPs is larger than their size, we can treat NPs as point-like sources of heat. Then, the heat source in the thermal equation (1) can be written as

$$Q(\mathbf{r},t) = \sum_{n} q_n(t) \delta(\mathbf{r} - \mathbf{r}_n),$$

where the coefficients  $q_n(t)$  describe the heat produced by the n-Au NP. The thermal state of the system will approach the steady-state solution of Eq. 1 for times  $t\gg l/K_{\rm matrix}$ , where l is the size of the NP complex and  $K_{\rm matrix}$  is the thermal diffusivity of the matrix. For typical parameters of polymers and  $l=1000~{\rm nm}=1~{\rm \mu m}$ , we obtain an estimate  $l/K_{\rm matrix}\approx 5~{\rm \mu s}$ . This estimate tells us that the thermal enhancement in a 1  ${\rm \mu m}$  superstructure can be achieved with laser pulses longer than 5  ${\rm \mu s}$ . In a superstructure of size l, the temperature can be estimated by an integral:

$$\Delta T_{\rm tot}(\mathbf{r}) = \sum_{n} \frac{q_n}{4\pi k_0} \frac{1}{|\mathbf{r} - \mathbf{r}_n|} \approx \frac{q_0}{4\pi k_0} \int_{V} \frac{D(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}',$$

where  $D(\mathbf{r})$  is the spatial density of identical NPs with  $q_n = q_0$ . For the temperature inside a superstructure of arbitrary dimensionality m, we obtain estimates in the limit  $N_{\rm NP}^{1/m} \gg 1$ :

$$\begin{split} & \Delta T_{\rm tot}(\mathbf{r}) \approx \Delta T_{\rm max,0} \frac{R_{\rm Au}}{\Delta} N_{\rm NP}^{\frac{m-1}{m}} (m=2 \text{ and } 3), \\ & \Delta T_{\rm tot}(\mathbf{r}) \approx \Delta T_{\rm max,0} \frac{R_{\rm Au}}{\Delta} \ln[N_{\rm NP}] (m=1), \end{split}$$

where  $\Delta T_{\rm max}$ ,0 is the temperature increase at the surface of NP for the case  $N_{\rm NP}=1$ ; this temperature is given by Eq. 4.  $\Delta$  and  $N_{\rm NP}$  are the average distance between NPs and the total number of NPs in a complex. The index m is 1, 2, and 3 for the 1D, 2D, and 3D superstructures, correspondingly. We can see from the above estimate that temperature grows with the number of NPs.



We now consider  $N_{\rm NP}$  nanoparticles on a surface between two mediums, water and substrate. The stationary solution of the heat equation for a NP at the boundary of two mediums is given by Eq. 3 with the substitution  $k_0 \to \bar{k}_0 = (k_{\rm water} + k_{\rm substrate})/2$ . Figure 5 shows calculated temperature in the center of a square array of 16 NPs (4 × 4) on the boundary of polymer and water. The distance between NPs is equal to  $\Delta = 150$  nm and their radii are 30 nm. We can see a strong increase of temperature in the NP complex (red curve in Fig. 5) compared to the case of a single NP (blue curve). Just recently the experimental study [8] demonstrated that the amount of generated heat becomes strongly increased in the NP complexes composed of several Au NPs.

### Electric-field enhancement in the NP system

Au NPs also interact through the electric fields. At large distances, the interaction is dipole–dipole; at small distances, it has a multipole character. Now we examine what happens with heat produced by two Au NPs interacting via Coulomb fields. In this paper, we will neglect the retardation effects; the latter is valid if the size of a system is less than the photon wavelength. Heat realized by the system per unit time is given by

$$Q_{\text{tot}}(\mathbf{r},t) = -\frac{1}{2} \text{Re} \left[ i\omega \frac{\varepsilon_{\text{Au}}(\omega) - 1}{4\pi} \right] \sum_{n=1,2} \int_{V_n} \tilde{\mathbf{E}}(\mathbf{r}) \tilde{\mathbf{E}}^*(\mathbf{r}) d^3 \mathbf{r},$$

where the summation is taken over two NPs with n=1 and 2. For numerical calculations of electric field, we used the method of multipole expansion of surface

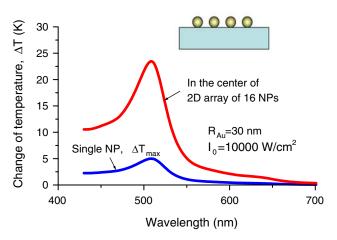


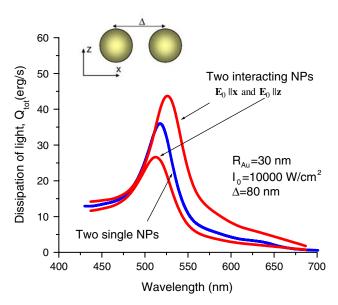
Fig. 5 Calculated temperature increase in the center of a square array of 16 NPs  $(4 \times 4)$  on the boundary of polymer and water. Inset: Model of Au NP complex

charges on NPs [16]. For the matrix, we assume a polymer with dielectric constant  $\varepsilon_0 = 2.3$ . We see in Fig. 6 that the total heat of two interacting NPs depends on the polarization of light. If the electric field of incident light is polarized along the "molecular" axis ( $\mathbf{x}$ ), the total heat is increased. In the cases  $\mathbf{E}_0 || \mathbf{y}$  and  $\mathbf{E}_0 || \mathbf{z}$ , the heat is reduced. This result shows that the heating effect can be enhanced or suppressed due to the inter-NP Coulomb interaction.

A random system of NPs can have "hot" spots where the electric field and heating intensity are greatly enhanced. A similar situation was observed in the classical experiments on surface enhanced Raman scattering (see e.g. [17]). The effect of hot spots can be used to create very strong heating in certain parts of a NP superstructure. One example is a system of three NPs shown in the inset of Fig. 7. Two large NPs (n = 1 and 2) play a role of amplifiers, whereas a smaller NP (n = 3) is a "heater". The data show that for  $\mathbf{E}_0 || x$ , the heating rate of the NP3 is strongly enhanced whereas for the other configurations it becomes slightly decreased. Such a collective effect of NPs can be used to strongly increase the heating intensity in certain points of a superstructure.

### **Conclusions**

We studied the effect of heating in the system composed of Au NPs, water, ice, and polymer. Au NPs



**Fig. 6** Calculated rate of light energy dissipation in the system of two Au NPs for different polarizations of incident photons. We also show the dissipation rate of two NPs in the limit  $\Delta \to \infty$ . Inset: Geometry of the system



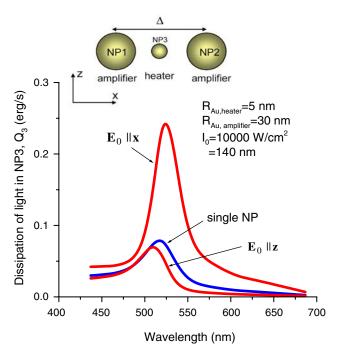


Fig. 7 Calculated rate of light energy dissipation in the small NP3 in the presence of two large NPs (NP1 and 2). We also show the dissipation rate of NP3 in the limit  $\Delta \to \infty$ . Inset: Geometry of the system

excited resonantly with light can increase temperature and even melt a surrounding material. The collective effects in NP superstructures can be used to strongly amplify the heating effect and also to create local areas of high temperature, hot spots. The latter originates from collective plasmon resonances in a superstructure.

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